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# 1 Stochastic evaluation of annual micropollutant loads and 2 their uncertainties in separate storm sewers

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## 13 14 **Abstract:**

15 This article describes a stochastic method to calculate the annual pollutant loads and its  
16 application over several years at the outlet of three catchments drained by separate storm  
17 sewers. A stochastic methodology using Monte Carlo simulations is proposed for assessing  
18 annual pollutant load, as well as the associated uncertainties, from a few event sampling  
19 campaigns and/or continuous turbidity measurements (representative of the Total Suspended  
20 Solids concentration (TSS)). Indeed, in the latter case, the proposed method takes into account  
21 the correlation between pollutants and TSS. The developed method was applied to data  
22 acquired within the French research project “INOGEV” (Innovations for a sustainable  
23 management of urban water) at the outlet of three urban catchments drained by separate storm  
24 sewers. Ten or so event sampling campaigns for a large range of pollutants (46 pollutants and  
25 2 conventional water quality parameters: TSS and total organic carbon (TOC)) are combined  
26 with hundreds of rainfall events for which, at least one among three continuously monitored  
27 parameters (rainfall intensity, flow rate and turbidity) is available.

28 Results obtained for the three catchments show that the annual pollutant loads can be  
29 estimated with uncertainties ranging from 10% to 60%, and the added value of turbidity  
30 monitoring for lowering the uncertainty is demonstrated. A low inter-annual and inter-site  
31 variability of pollutant loads, for many of studied pollutants, is observed with respect to the  
32 estimated uncertainties, and can be explained mainly by annual precipitation.

33  
34 **Keywords:** Stormwater; database; pollutant; annual load; turbidity; TSS; uncertainties;  
35 variability.

36

## 37 INTRODUCTION

38 In the case of separate storm sewers, runoff is usually discharged directly into the natural  
39 environment without any treatment. These discharges constitute a continuous and significant  
40 vector of pollutants towards receiving waters (Becouze-Lareure et al. 2011, Clark et al. 2007,  
41 Weiss et al. 2008, Zgheib et al. 2012). The reduction of these discharges is a major issue of  
42 the EU Water Framework Directive (WFD) (2013/39/EU) to achieve the “good ecological  
43 status” for all of Europe's surface waters and groundwater. This challenge requires accurate  
44 knowledge of pollutant loads discharged by separate sewer. Beyond the conventional water  
45 quality parameters (Total Suspended Solids (TSS); Chemical Oxygen Demand (COD); etc.)  
46 extensively studied over several decades, monitoring of priority and/or emerging substances  
47 has become an important issue in Europe to meet the requirements of the WFD (Sebastian et  
48 al. 2011). Due to financial costs, operational and technical issues, the assessment of pollutant  
49 loads is constrained by a lack of suitable measuring devices. Monitoring is frequently carried  
50 out by taking samples for subsequent analysis in the laboratory. Analytical methods are  
51 standardized but still pollutant dependant. Yet, the sampling process has some major  
52 drawbacks, among which the limited number of samples which can practically be handled due  
53 to random occurrence of rain events, frequent maintenance, etc. Indeed, monitoring programs  
54 prove to be very costly and require considerable staff time. Only a limited number of  
55 campaigns (generally less than 5) are thus carried out during a given year (Gromaire et al.  
56 2007) for operational purposes, and data are usually pooled to derive an Annual (or Site-  
57 specific) discharge-weighted (or arithmetic) Mean Concentration SMC, whose value is then  
58 multiplied by the total runoff volume of the considered period to assess pollutant loads. This  
59 method induces large uncertainty values (Mourad et al. 2005).

60  
61 Besides these considerations TSS have been revealed as the predominant pollutant vector in  
62 sewer systems (Ashley et al. 2005, Zgheib et al. 2012). In fact, for some pollutants such as  
63 PAH, PCB and metals, TSS is a significant vector, while isn't for other pollutants such as  
64 Octylphenol OP, TSS is not the significant vector (Zgheib et al. 2012).

65  
66 Continuous turbidity measurements can now provide recordings which are representative of  
67 the TSS concentration. Actually, turbidity can be translated into TSS concentration by using  
68 an average TSS-Turbidity relationship at different time-scales (Hannouche et al. 2011, Lacour  
69 et al. 2009, Langeveld et al. 2005, Metadier and Bertrand-Krajewski 2012). TSS  
70 concentration time-series are thus made available. The use of continuous measurement data  
71 (rain intensity, flow rate, turbidity), in addition to a limited number of laboratory analysis by  
72 sampling, therefore enables a more accurate assessment of the annual micropollutants flux.

73  
74 In this context, the “INOGEV” project (*Innovations for a sustainable management of urban*  
75 *water*) was launched in early 2010 by the national network of French observatories in urban  
76 hydrology “SOERE URBIS” (*A long-term Observation System for research and*  
77 *Experimentation on urban environment*) combining the works of “OPUR” in Paris  
78 (*Observatory of Urban Pollutants in Île-de- France/Paris region, since 1994*), “OTHU” in  
79 Lyon (*Field Observatory for Urban Water Management in Lyon-France, since 1999*) and  
80 “ONEVU” in Nantes (*Observatory of urban environments of Nantes- France, since 2006*).  
81 This project aimed at improving the knowledge and control of the contamination of urban  
82 stormwater in a multidisciplinary approach as regards scientific research, operational practices  
83 and social understanding. By harmonizing scientific approaches and monitoring  
84 methodologies (pollutants, sampling, analytical methods and results interpretation) at the  
85 scale of three urban districts featuring distinct land use patterns and contexts, a new extended

86 French dataset has been built for a large range of pollutants at the event scale (Gasperi et al.  
 87 2014). In addition, the observatories had formerly provided some statistically representative  
 88 databases for water flow rate and turbidity measurements for several years at the outlet of two  
 89 of the three studied catchments.

90  
 91 In this paper, a combined approach was adopted coupling the new dataset of pollutant  
 92 concentrations and available recordings of hydrological and water quality parameters (rainfall  
 93 intensity, flow rate, turbidity), to assess annual pollutant loads as well as the associated  
 94 uncertainties. First the databases used are briefly presented. Then, the methodology developed  
 95 to assess the annual loads and their uncertainty for a given pollutant including the underlying  
 96 hypotheses is described. Results obtained are then discussed and compared between the three  
 97 sites.

## 98 **EXPERIMENTAL DATA**

### 99 **Sites description**

100 Three experimental sites drained by a separate sewer systems (*Sucy* in Île-De-France/Paris  
 101 region, *Chassieu* in Lyon and *Pin Sec* in Nantes) were considered. *Table 1* summarizes the  
 102 main characteristics and the available databases at the three sites. Their areas range from 30 to  
 103 228 ha and their runoff coefficients (*RC*) vary between 22 (*Sucy*) to 30% (*Chassieu*).  
 104 *Chassieu* is an industrial catchment while other catchments are residential with mostly small  
 105 private houses and limited commercial and professional activity (small shops and services) at  
 106 *Sucy* catchment, and mainly collective buildings and private houses at *Pin Sec* catchment. On  
 107 the whole, most of buildings and houses were built between the years 1970 and 1980.

108  
 109 **Table 1: Sites and databases available**

Sites	Location	Area	RC <sup>1</sup>	Land use	Slope	Available data
<i>Sucy</i>	Paris, South- East	228 ha	0.22	Residential	0.2%	- Continuous rainfall intensity, flow and turbidity measurements (Time step=2 min; 2011-2012): 121/220 rain events <sup>(2, a)</sup> ; - Sampled rainfall events <sup>(3)</sup> : 24 (7-10 <sup>(4)</sup> )
<i>Chassieu</i>	Lyon, East	185 ha	0.30	Industrial	0.4%	- Continuous rainfall intensity, flow and turbidity measurements (Time step=2 min; 2004-2008): 263/655 rain events <sup>(2, a)</sup> ; - Sampled rainfall events <sup>(3)</sup> : 7 (2-5 <sup>(4)</sup> )
<i>Pin Sec</i>	Nantes, North- East	30 ha	0.26	Residential and collective housing	1.0%	- Continuous rain intensity and flow measurements (Time step=5 min; 2011-2012): 198/214 rain events (2, b); - Sampled rainfall events (3): 18 (7-15 (4))

110 (1) *RC* = runoff coefficient (see Precipitation – volume model (Model M1) for more information), (2) number of rainfall  
 111 events with: (a), valid flow and turbidity measurements compared to all identified rain events, (b) valid flow  
 112 measurements compared to all identified rain events (no turbidity measurement at *Pin Sec* site); (3) Number of rainfall  
 113 events sampled at each site with measurements of global parameters; (4) Number of rain events analyzed for each group  
 114 of micropollutants.

### 115 **Available monitoring data**

#### 116 **Sampled rainfall events and measured pollutants**

117 Depending on the site under consideration, between 7 and 24 rainfall events were sampled  
 118 from July 2011 to May 2013 with automatic samplers controlled by a flow-meter to obtain  
 119 flow proportional event mean concentrations (EMC). The sampling equipment and field blank  
 120 procedures were harmonized between observatories and described in (Gasperi et al. 2014).

121

122 The main characteristics of these events such as precipitation depth ( $H$  in  $mm$ ), mean and max  
123 intensity in 5 min ( $I_{\text{mean}}$  and  $I_{\text{max}}$  in  $mm.h^{-1}$ ) and preceding dry weather period (PDWP in days)  
124 are given in *Table 6* in supplementary materials section. On the whole, these rainfall events  
125 feature relatively low rainfall intensities, with no extreme rainfall amounts collected.

126  
127 Conventional water quality parameters, such as TSS and total dissolved and particulate  
128 organic carbon (TOC, DOC and POC), were analyzed for each rain event sampled. A total of  
129 46 micropollutants were monitored for 2 to 15 rainfall events, including 13 metals, 16  
130 polycyclic aromatic hydrocarbons (PAH), 9 polybromodiphenylethers (PBDE), bisphenol A  
131 (BPA) and 7 alkylphenols (APnEOs). The full list of targeted molecules and the usual  
132 abbreviations are listed extensively in *Table 7* supplementary materials section.

### 133 **Continuous measurements**

134 All sites are equipped with monitoring stations for rainfall intensity, flow rate. Rainfall  
135 intensities at each catchment area were measured by tipping bucket rain gauges. Raw data  
136 were converted into 5 min time step time series. The flow rates are derived from both water  
137 level and flow velocity monitoring at the outlet of each catchment. Turbidity was monitored  
138 continuously at *Sucy* and *Chassieu*, with two redundant turbidity sensors at a 2 min time step:

- 139 - In *Sucy* site, 2 turbidimeters (Ponselle brand, TU-TRANS-NA) with attenuation at 880 nm  
140 and calibration using formazin (range=0-2000 FAU (Formazin Attenuation Unit)) are  
141 used. The sensors are installed in the storm sewer pipe, next to the point of flow  
142 measurement.
- 143 - In *Chassieu* site, 2 turbidimeters (one Endress-Hauser W CUS31 and one Dr Lange  
144 Solitax) with nephelometry at 860 nm and calibration using Formazin (range =0-4000  
145 FNU (Formazin Nephelometry Unit)) are used. The turbidity is measured in an off-line  
146 monitoring flume installed in a shelter located above ground (Metadier and Bertrand-  
147 Krajewski 2012). Water is pumped from the sewer into the flume by a peristaltic pump at  
148 approximately 1 L/s and a suction velocity of approximately 1 m/s to avoid settling and  
149 particle segregation in the pumping tube.

150  
151 Turbidity data were processed and validated by using redundancy in *Sucy* (Lacour et al. 2009)  
152 site or by using the method detailed in (Mourad and Bertrand-Kralewski 2002) in *Chassieu*  
153 site.

154  
155 Storm events are identified using flow rate and rainfall intensity. The beginning of the event is  
156 given by the rise of the flow rate signal whereas the end of the event is given by the return to  
157 the dry weather base-flow attributed to groundwater infiltration. In a second step, the runoff  
158 events identified are compared to rainfall data to eliminate all hydrographs which correspond  
159 to a precipitation depth lower than  $0.5 mm$  ( $<$  Initial loss, see Precipitation – volume model  
160 (Model M1) for more information). During the years 2011 and 2012: i) 220 rain events have  
161 been identified for *Sucy* site including 121 rainfall events with valid flow and turbidity  
162 measurements, ii) and 214 rain events for *Pin Sec* site among which 198 events possess valid  
163 flow measurements). Over the period 2004–2008 in *Chassieu* site, the final validated database  
164 (flow and turbidity) contains 263 events among 655 identified rain events (*Table 1*). Indeed,  
165 data acquired at this site between 2011 and 2012 was not exploitable because of the failures of  
166 the peristaltic pump.

167  
168 The main characteristics of these rainfall events are given in *Table 2*. The characteristics of  
169 these rainfall events are with the same magnitude as those sampled during the pollutant  
170 sampling campaigns.

171  
172

**Table 2: Main rainfall characteristics of the identified rain events on the three study sites (d<sub>10</sub>-d<sub>50</sub>-d<sub>90</sub>).**

	H (mm) <sup>(1)</sup>	Duration (h)	I <sub>mean</sub> (mm.h <sup>-1</sup> )	I <sub>max</sub> (mm.h <sup>-1</sup> ) <sup>(2)</sup>	PDWP <sup>(3)</sup>
<i>Sucy</i> (n=121)	1.4-5.0-12.7	1.0-4.7-13.0	0.6-1.3-2.7	2.4-4.8-21.6	0.22-1.29-5.12
<i>Chassieu</i> (n=263)	1.0-2.4-14.7	0.7-3.5-13.0	0.3-1.1-2.8	1.5-4.4-17.5	0.25-0.65-5.6
<i>Pin Sec</i> (n=198)	1.3-3.2-13.0	0.7-2.2-11.8	0.8-2.2-3.6	3.1-7.3-15.5	0.11-0.97-9.54

1) Precipitation depth; 2) I<sub>max</sub> evaluated over 5-min intervals; 3) Preceding dry weather period, in days.

### 173 TSS-Turbidity correlation functions and uncertainties

174 Previous research demonstrated that linear or polynomial function can be used to estimate  
175 TSS concentration from turbidity (Hannouche et al. 2011, Metadier and Bertrand-Krajewski  
176 2012).

177 For *Sucy*, the discharge-weighted event mean turbidity (EMT) was calculated from the  
178 continuous and validated turbidity measurements for 14 rainfall events among the 24 rainfall  
179 events sampled in *Sucy* site. The 14 pairs (EMT, TSS) obtained allowed us to build the TSS-  
180 turbidity linear function (*Figure 1*, (a);  $TSS_{(mg/l)}=f(EMT_{(FAU)})=31.9+0.45EMT$ , (Equation 1))  
181 at the event scale. For each rainfall event *j* for which there is a validated turbidity  
182 pollutograph ( $T_{ij}$ ) (*i* is an index of the time step) and flow rate hydrograph ( $Q_{ij}$ ), a discharge-

183 weighted event mean turbidity is calculated  $T_j \approx \frac{\sum_{i=1}^{n_j} T_{ji} \times Q_{ji} \times \Delta t_{ji}}{\sum_{i=1}^{n_j} Q_{ji} \times \Delta t_{ji}}$  (Equation 2) and then

184 transformed into TSS event mass by applying the TSS-turbidity linear function established on  
185 this site. Finally, the residual error implied by this conversion is assessed by assuming that  
186 residual errors follow a normal distribution with same variance derived from residues observed  
187 for calibration data (Hannouche et al. 2011).

188  
189 About sixty grab sample were taken in *Chassieu* site by (Metadier and Bertrand-Krajewski  
190 2012) during wet weather conditions between 2002 and 2008 (we have no information on the  
191 number of sampled events). For each sample, 25 repeated turbidity measurements and  
192 triplicate TSS analysis according to usual standards methods are carried out, including  
193 assessment of uncertainties. These have allowed to build a second degree polynomial function  
194 ( $TSS_{(mg/l)}=12.9+0.7*T_{(FNU)}+7.8e-4*T_{(FNU)}^2$ , (Equation 3)) by means of Williamson weighted  
195 least squares regression method accounting for uncertainties in both coordinates (TSS and  
196 turbidity) A detailed description of this method and uncertainty estimation are reported in  
197 (Metadier and Bertrand-Krajewski 2011). The obtained correlation function in *Chassieu* is  
198 given in *Figure 1*, (b).

199 Note that the difference in procedure for estimation of TSS concentration at both sites is due  
200 to the methods of turbidity measurements and to available TSS-Turbidity data on each site.

201

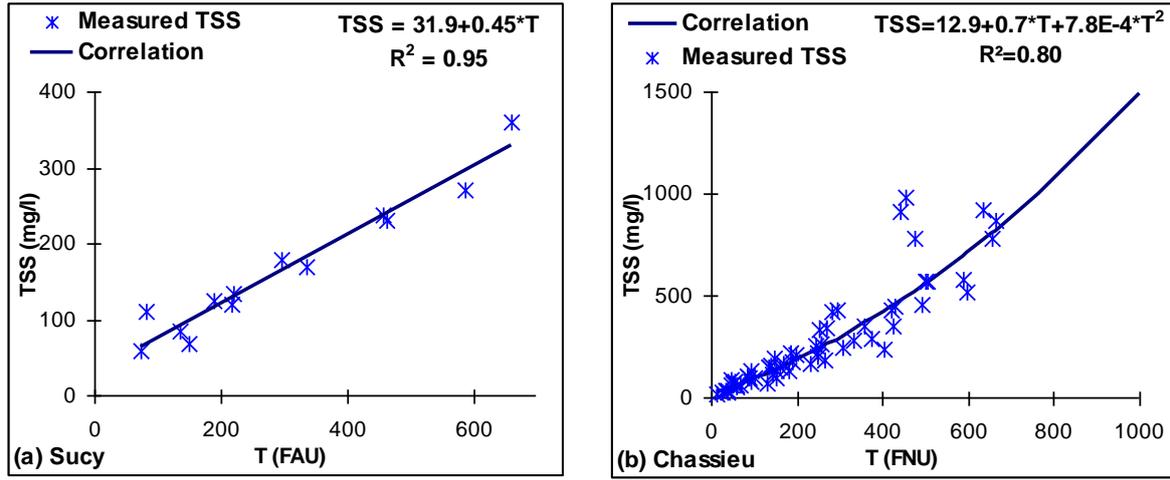


Figure 1: TSS-Turbidity correlation functions: (a) *Sucy* ; (b) *Chassieu*

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The two correlation functions on both sites are different. This may be mainly due to measuring and calculation methods used at each site (attenuation in *Sucy* and nephelometry in *Chassieu*). Indeed, at the *Chassieu* site, this relationship was established by (Metadier and Bertrand-Krajewski 2011) for instantaneous samples with turbidity measured in nephelometry. While on the *Sucy* site, we calculated event mean turbidity for rain events (which are less variable than those of instantaneous turbidities), for which the event mean concentration and turbidity pollutograph are known. Moreover, although the y-intercept (measurement offset) at *Sucy* site is quite high (31.9 mg/l TSS at 0 FAU), its variability at 95% prediction intervals is approximately  $\pm 25$  mg/l TSS. It should be noted that this relationship was established for a range of turbidity between 70 and 660 FAU and was used for turbidities varying between 60 and 700 FAU (average value = 250 FAU).

## 214 CALCULATION METHOD

215 In the case of a discrete sampling of all events for a given year, the pollutant loads  $M_{pol}$  for  
216 year  $k$  could be calculated by sequential summation of loads  $M_{j\ pol}$  of all rainfall events  
217 (indexed by  $j$  with a number  $N_{events}$ ) that occurred during this year and by sequential  
218 summation at time step  $i$  (with a number  $n_j$  time step), over the duration of each event. It is  
219 further assumed that the pollutant load transited during dry weather periods (improper  
220 connections, infiltration...) is negligible compared with the one transported during wet  
221 weather periods throughout one year. So:

$$222 \quad M_{pol} = \sum_{j=1}^{N_{events}} M_{polj} \approx \sum_{j=1}^{N_{events}} \sum_{i=1}^{n_j} C_{T-pol_{ji}} \times Q_{ji} \times \Delta t_{ji} \quad (\text{Equation 4})$$

223 With  $Q_{ji}$  = flow rate and  $C_{T-pol_{ji}}$  = total (i.e. dissolved and particulate) pollutant concentration  
224 at time step  $i$  ( $\Delta t_{ji}$ ) during the event  $j$ . The symbol ( $\approx$ ) indicates that there is a discretization  
225 error.

226  
227 Thus, estimating the mass  $M_{j\ pol}$  using the above formula requires knowledge of the  
228 dynamics of total pollutant concentration  $C_{T-pol}$  and flow rate at each time step. Actually, the  
229 details of the dynamics of pollutant loads within a rainfall event is not considered by itself,  
230 but only as a mean to get an integrated value of the product  $Q_{ji} \times C_{T-pol_{ji}} \times \Delta t_{ji}$  over the

231 duration of the rainfall event. Thus an analysis performed on a flow-weighted composite  
232 sample representative of the entire rainfall event  $j$  is sufficient for estimating the total  
233 pollutant EMC  $C_{T-pol_j}$ , and assessing the event load  $M_{j-pol}$  of rainfall event  $j$  as

234  $M_{j-pol} = C_{T-pol_j} \times V_j$  (Equation 5) with  $V_j$  is the volume of water transported during the  
235 rainfall  $j$ .

236 Continuous monitoring of flow rate is commonly available, and the equation 5 can be applied  
237 to events for which monitoring was carried out for providing  $C_{T-pol_j}$ . But pollutant  
238 concentrations data are always very scarce, due to sampling and analysis constraints. So we  
239 investigate the possible combination of continuous monitoring of some parameters with  
240 analyses performed on flow rate averaged event mean samples collected from a few rain  
241 events. We especially focus on the added value of turbidity monitoring for improving the  
242 assessment of pollutant annual load for pollutants which are significantly correlated with TSS  
243 EMC.

244  
245 In this scope, we distinguish two types of pollutants according to the dependence of their total  
246 concentrations on TSS concentration. Indeed, the total pollutant concentration  $C_{T-pol}$  is  
247 expressed as the sum of dissolved  $C_{D-pol}(unit/l)$  and particulate  $C_{P-pol}(unit/l)$   
248 concentrations ( $unit \sim mg$  or  $\mu g$  or  $ng$ ):

249  $C_{T-pol} = C_{D-pol} + C_{P-pol} = C_{D-pol} + \tau \times TSS$  (Equation 6), with  $TSS(mg/l)$  is TSS EMC  
250 concentration and  $\tau$  is the particle pollutant content ( $unit/mg$  TSS, i.e.  $\tau =$  particulate  
251 concentration / TSS concentration =  $C_{P-pol}/TSS$ ).

252  
253 The combination of pollutograph and hydrograph of a rainfall event  $j$  allows us to estimate the  
254 TSS EMC of this rainfall event using (equations 1, 2 and 3).

255  
256 After identifying the rainfall events in a given year (using precipitation and flow rate time  
257 series), from one to four stochastic models are used to handle missing data and finally get an  
258 assessment of total pollutant EMC for a given pollutant for any event. Then, an annual flow  
259 weighted concentration is derived from the EMC values for all events in one particular year,  
260 and the process is repeated by the means of Monte-Carlo simulation to derive a mean value  
261 and a confidence interval for each considered pollutant.

## 262 **Model structures**

263 For a given event, two models are used to handle the lack of continuously monitored data:

- 264 1. A precipitation – volume model (model M1) to estimate a value and its uncertainty of  
265 the runoff volume of a rainfall event for which there is no flow rate measurement.
- 266 2. A TSS EMC model (model M2) to estimate the TSS EMC probability distribution of a  
267 rainfall event for which neither TSS EMC analysis nor turbidity measurements were  
268 available (either due to the lack of sensor or to a drift or failure of available sensors).

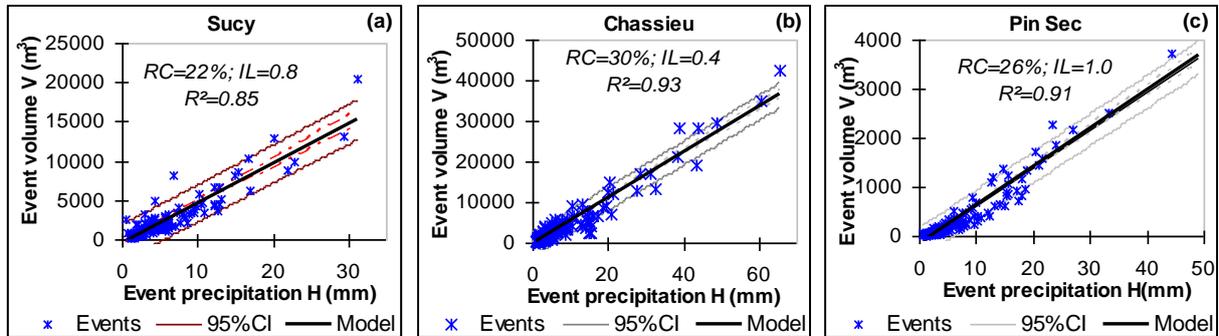
269  
270 In addition, two other models are used to extrapolate data from the few events sampled for  
271 pollutant EMC analysis to other events, where such analysis is missing:

- 272 3. M3 is used when no correlation between  $C_{P-pol}$  EMC and TSS EMC is identified, and  
273  $C_{T-pol}$  EMC.
- 274 4. M4 is used when a significant correlation between  $C_{P-pol}$  EMC and TSS EMC is  
275 identified and provides the probability distribution of  $C_{T-pol}$  EMC as the sum of  $C_{D-pol}$

276 EMC overall probability distribution and  $C_{P-pol}$  EMC probability distribution assessed  
 277 from TSS EMC value and  $\tau$ .  
 278 M2 and M3 models have no input variable and provide an overall distribution whereas M1  
 279 and M4 models use a measured variable (rainfall or TSS) as an input in a linear regression,  
 280 thus providing a conditional distribution.  
 281

## 282 Precipitation – volume model (Model M1)

283 The first model (M1) is a linear model using the runoff coefficient  $RC$  to estimate the event  
 284 volume  $V$  as a function of the precipitation  $H$  according to the relationship  
 285  $V = 10 \times A \times RC \times (H - IL)$  where  $IL$  is the initial loss (in mm) and  $A$  is the catchment  
 286 surface area (in ha). For a given catchment, model M1 was fitted by means of least squares  
 287 method using all the events for which simultaneous flow rate and rainfall intensity are  
 288 available. Figure 2 illustrates the runoff model ( $V = 10 \times A \times RC \times (H - IL)$ ) (Equation 7)  
 289 obtained on each site and the corresponding 95% prediction intervals (95% PI). The obtained  
 290 runoff coefficients  $RC$  are reported in Table 1 above.  
 291



292  
 293 **Figure 2: Runoff models and corresponding 95% CI (RC= runoff coefficient, IL = initial loss) for: (a)**  
 294 **Sucy, (b) Chassieu and (c) Pin Sec**

## 295 TSS EMC model (Model M2)

296 No model could be identified for linking the TSS EMC for a rainfall event to the  
 297 characteristics of this event (precipitation depth, rainfall intensity, preceding dry weather). A  
 298 probability distribution model (M2) was used instead and fitted to all TSS measures available  
 299 on a given site or derived from turbidity measurements. For a given site, the Kolmogorov-  
 300 Smirnov test was used to fit theoretical and TSS EMC empirical distributions at the 5% level.  
 301 Different simulations show that the lognormal distribution is well suited for describing the  
 302 TSS EMC (KS test,  $\alpha=5\%$ ). Hence, both the mean ( $m$ ) and standard deviation ( $SD$ ) of EMCs  
 303 (estimated distribution) have been calculated first in natural logarithm space ( $\mu$  and  $\sigma$  mean  
 304 and standard deviation of  $(\ln(TSS\ EMC))$ ) and then transformed into arithmetic space (Romeu  
 305 2002) using the formulas:  $m = \exp\left(\mu + \frac{\sigma^2}{2}\right)$  and  $SD = \sqrt{\exp(\sigma^2) - 1} \times m$  (Equations 8 & 9)  
 306 where  $\exp(x)$  is the exponential function of  $x$ . The parameters of fitted distributions for  
 307 different sites are summarized in Table 3.  
 308

309 **Table 3: Means and SD of the fitted lognormal distributions of TSS EMC and those of  $n$  rainfall events on**  
 310 **the three sites Sucy, Chassieu and Pin Sec**

Site	n	$\mu$	$\sigma$	m	SD	KS p-value <sup>(1)</sup>	$\overline{EMC}$ <sup>(2)</sup>	$\sigma_{EMC}$ <sup>(2)</sup>
Sucy	121	4.83	0.49	141	74	84%	141	73
Chassieu	263	4.63	0.79	140	130	87%	144	144

<i>Pin Sec</i>	18	4.57	0.76	128	114	82%	124	85
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(1) p-value for Kolmogorov-Smirnov test; (2) mean and SD calculated on the n rainfall events

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Note that the TSS EMCs on both *Sucy* and *Chassieu* sites were calculated from the turbidity data, while those of *Pin Sec* site are those of the measurement campaigns (Table 6). Kruskal-Wallis statistical test shows that the distributions of TSS EMCs are not significantly different between the three sites ( $\alpha = 5\%$  and p-value=17%). In addition, the same test shows that there is no significant difference between the distribution of TSS EMC from one year to another in the same site (*Sucy* and *Chassieu* sites).

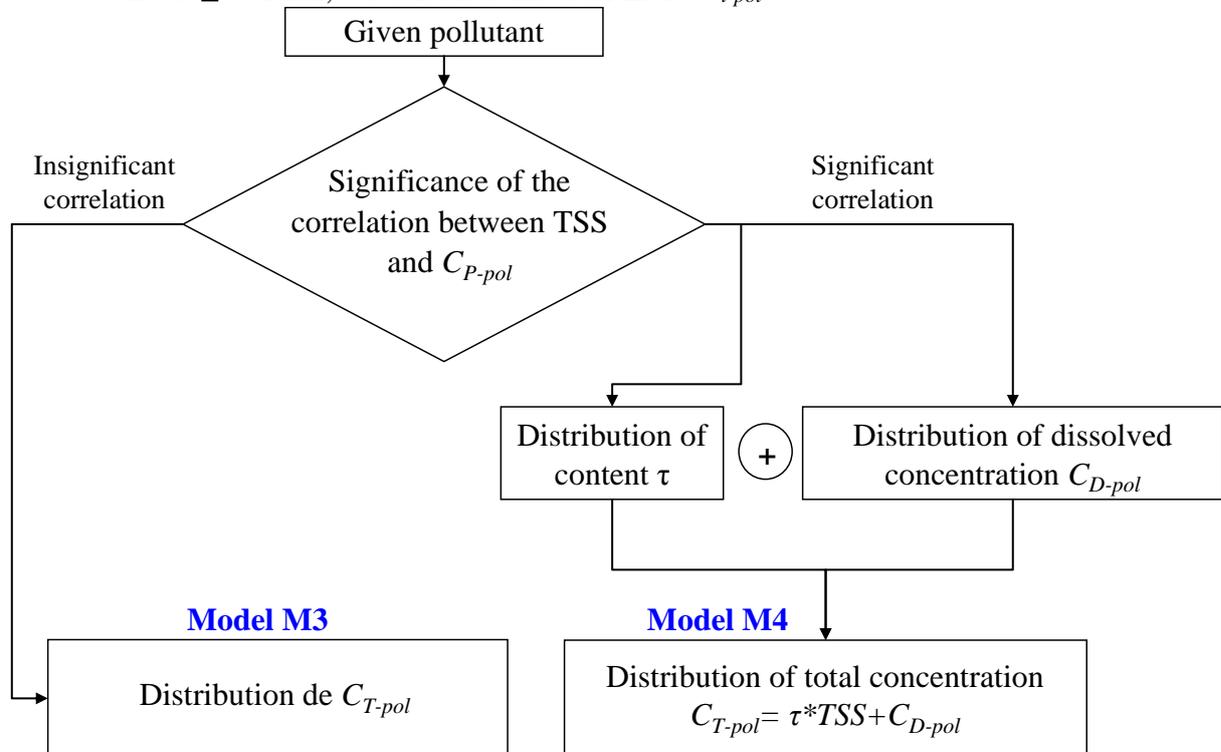
### 319 **C<sub>T-pol</sub> EMC models (Models M3 and M4)**

320 As for TSS, no model was identified for assessing the total pollutant EMC C<sub>T-pol</sub> according to  
321 the characteristics of the corresponding rainfall event. So, a distribution model was applied.  
322 Figure 3 illustrates the methodology of calibration of the distribution model of C<sub>T-pol</sub> EMC.

323

324 First of all, the significance of the correlation coefficient ( $\rho_{TSS-pol\ part}$ ) between TSS EMC and  
325 particulate concentration C<sub>P-pol</sub> EMC was tested for a given pollutant by using Pearson  
326 parametric test for normal distribution or Spearman nonparametric test otherwise ( $\alpha=5\%$  for  
327 all these tests). The significance of this correlation leads the choice between two models:

- 328 1. No significant correlation: a distribution of C<sub>t-pol</sub> EMC (in  $\mu g/l$ ) (model M3) is used.  
329 Model distributions are then fitted, using KS test ( $\alpha=5\%$ ) when the number of events  
330 is greater than or equal to 6 (Romeu 2003);
- 331 2. Significant correlation: a model (model M4) is used, which results from a distribution  
332 of contents  $\tau$  (e.g.  $\mu g/mg$  TSS), a value of TSS EMC (e.g.  $mg/l$ ) (obtained by turbidity  
333 measurements or M2 model) and a distribution of dissolved concentrations C<sub>D-pol</sub>  
334 EMC (e.g.  $\mu g/l$ ). The distributions of  $\tau$  and of C<sub>D-pol</sub> EMC are fitted if the number of  
335 events is  $\geq 6$ . Then, we calculate the total EMC C<sub>t-pol</sub>.



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Figure 3: Methodology for deriving the distribution model of EMC for a given pollutant

339 Furthermore, the rather low number of sampled rainfall events (*Table 1*) is not practical to fit  
340 a distribution of EMC for a given pollutant and a given site, especially in the case of *Chassieu*  
341 site (2 to 5 measurements per pollutant, *Table 1*). To solve this problem, the data from all  
342 three sites were pooled when no significant site-to-site difference between the EMC  
343 distributions of this pollutant was detected. Indeed, the homogeneity of  $C_{T-pol}$  EMC for model  
344 M3 (or  $C_{D-pol}$  EMC or  $\tau$  for model M4) for a given pollutant between three sites is verified at  
345 the level of 5% (ANOVA parametric test if the homogeneity of variance (Levene's test) and  
346 normality (Shapiro-Wilk normality test) are accepted, Kruskal-Wallis non-parametric test  
347 otherwise (often used as an alternative to the ANOVA where the assumption of normality is  
348 not acceptable)). In the case of rejection of the hypothesis of homogeneity of  $C_{T-pol}$  ( $C_{D-pol}$   
349 EMC or  $\tau$ ), the Siegel–Tukey test of multiple comparisons is applied to find homogeneous  
350 groups of sites for a given pollutant. All these statistical tests were performed with the  
351 statistical software XLSTAT® (version 2009.3.02, Addinsoft, New York,  
352 <http://www.xlstat.com>).

353  
354 Kolmogorov-Smirnov test shows that lognormal distributions are well suited to describe  
355 pollutants EMCs at the level of 5%: total  $C_{T-pol}$ , dissolved  $C_{d-pol}$  and particle contents  $\tau$  (KS p-  
356 value  $\geq 20\%$ ). These results are in good agreement with those observed in the literature (EPA  
357 2005, Francey et al. 2010, Mourad et al. 2005, Smullen et al. 1999).

358  $C_{T-pol}$  EMC for the different pollutants and groups of pollutants were hence estimated. Indeed,  
359 the results for each metal are presented. By contrast, PAHs are presented on the basis of total  
360 concentrations, i.e.  $\sum_{16} PAH$  (EPA 2005) or  $\sum_{13} PAH$  (excluding volatile PAH: N, Acen and  
361 Acyl). For PBDE, the results are presented for  $\sum_9 PBDE$  and deca-BDE (BDE-209) which  
362 displayed the highest concentrations compared to other PBDE. The results of BPA, of  
363 octylphenols ( $\sum OP$ , octylphenol and octylphenol ethoxylates) and nonylphenols ( $\sum NP$ ,  
364 nonylphenol and nonylphenol ethoxylates) are also presented.

365  
366 Figure 4 and ***Erreur ! Source du renvoi introuvable.*** illustrate in the approach applied for  
367 two pollutants:  $\sum OP$  and Pb. The method presented above is discussed in both figures.

368 Parameters of the different distributions for models M3 and M4 in natural logarithm space ( $\mu$   
369 and  $\sigma$ ) are reported in *Table 8* in supplementary materials. For more details about the intra  
370 and inter-site variability of concentration for a given pollutant, an analysis with a comparison  
371 with literature, is detailed in (Gasperi et al. 2014).

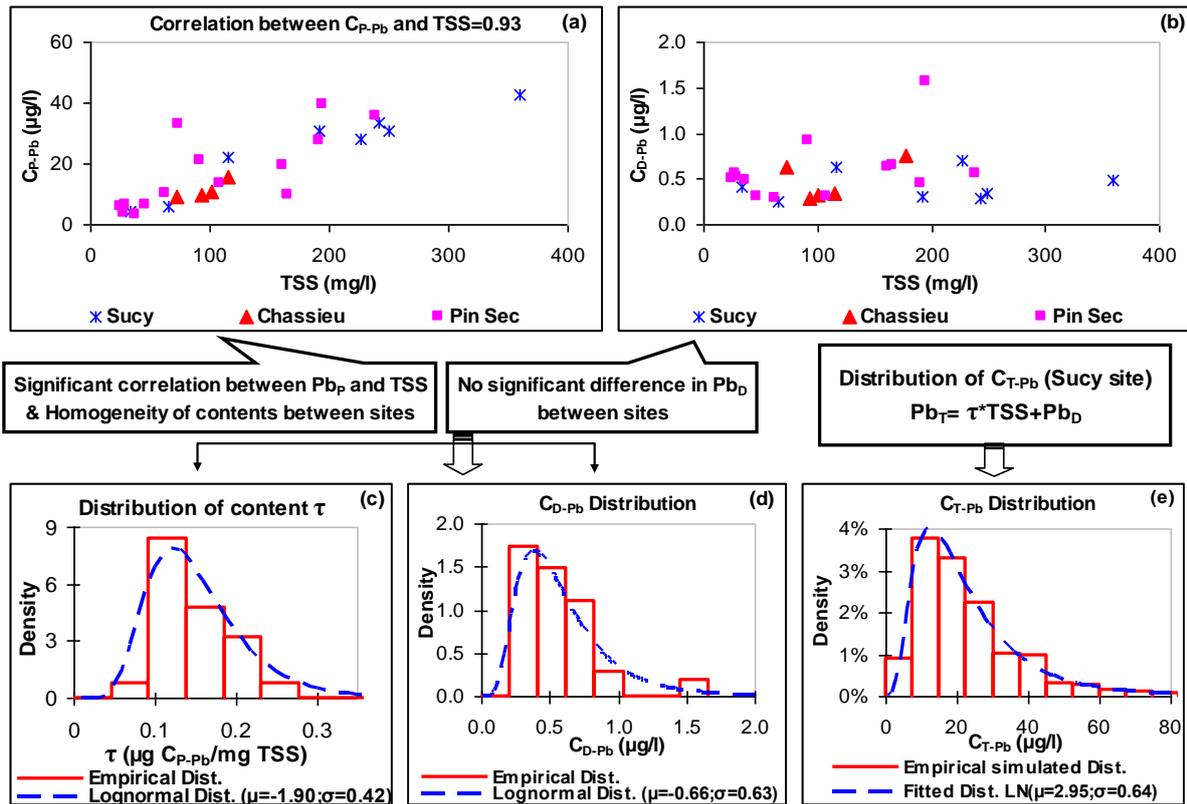


Figure 4: Example of the construction of the model of CT-Pol EMC (M4) for Pb; (e): case of Sucy site

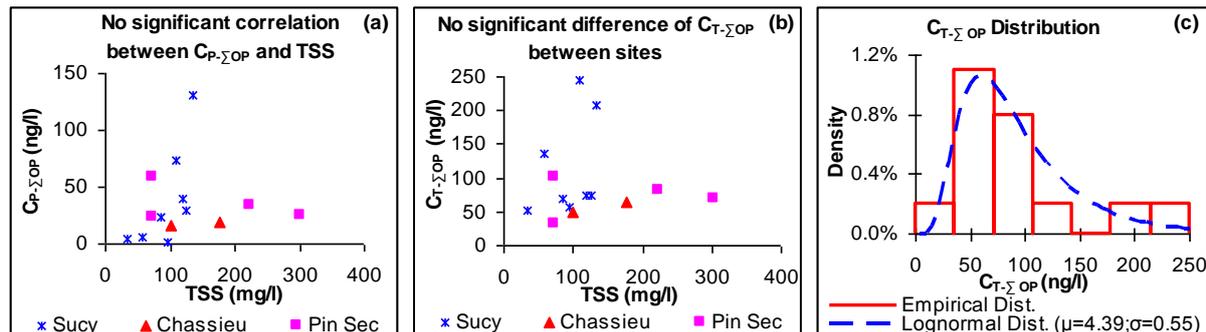


Figure 5: Example of the construction of the model of CT-Pol EMC (M3) for  $\Sigma OP$

When validated, the lognormal distribution obtained by model M3 is directly used in the calculation of the annual load of this pollutant (example *Erreur ! Source du renvoi introuvable. c*)).

Alternatively, two independent simulations (condition of independence has been checked using the partition coefficient  $K_d = \tau / C_{D-pol}$ ) using obtained lognormal distributions of  $\tau$  (Figure 4 (c)) and total  $C_{D-pol}$  (Figure 4 (d)) for a given pollutant are coupled with a TSS concentration (calculated using turbidity or simulated using model M2) to calculate a  $C_{T-pol}$  of this pollutant for the corresponding event (Figure 4 (e)).

### Monte Carlo simulations

Monte Carlo simulations are used to combine the different models detailed above for each particular event in a given year and propagate the probability distributions from each model involved for each event to the annual average values and quantify the associated uncertainties. Figure 6 illustrates the methodology for assessing pollutant annual load  $M_{Pol}$  for a given year and for a given pollutant using a Monte Carlo simulation (ISO/IEC 2008). Note that the

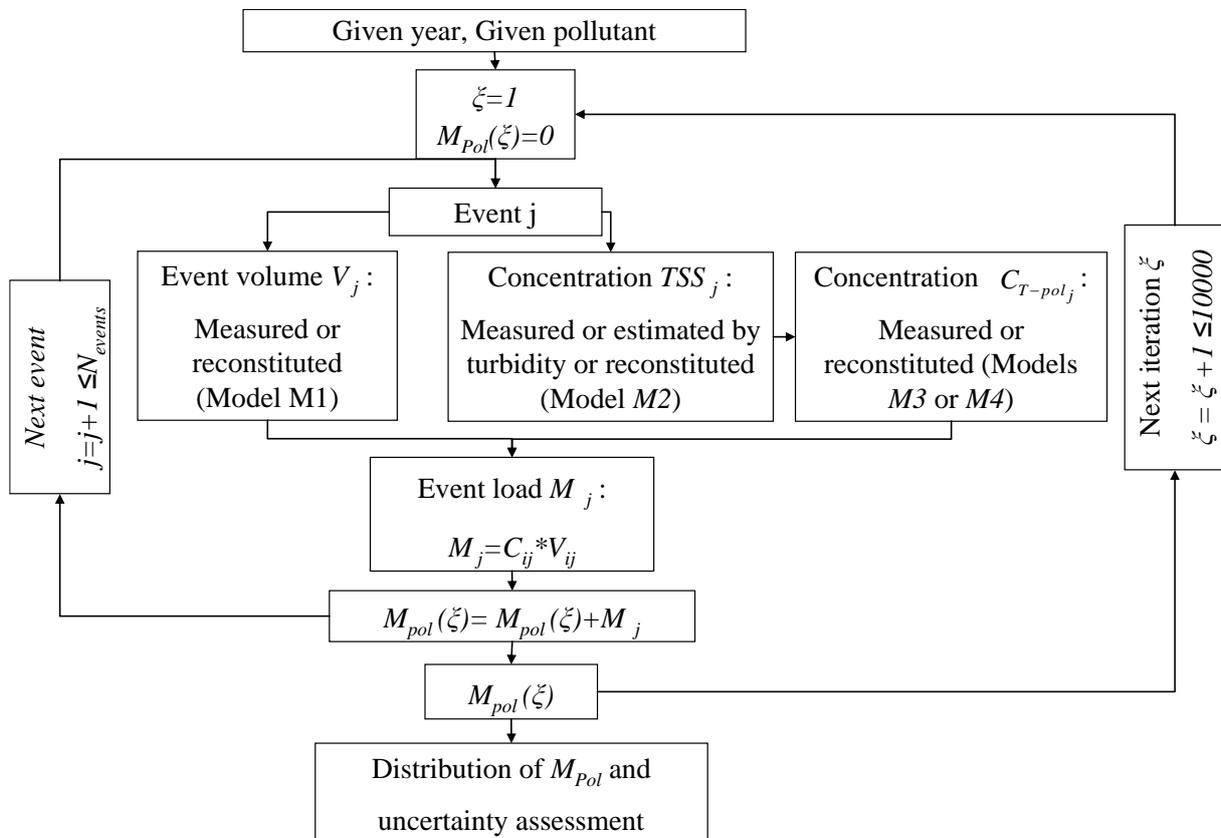
392 hypothesis of independence between the event volume and concentration was checked for  
 393 sampled events.

394 Then, the masses of all the events of this year for a given pollutant are summed up. This  
 395 process was then reiterated 10,000 times for each year to obtain a probability distribution of  
 396 annual load  $M_{Pol}$ . The average pollutant annual load and the corresponding uncertainties are  
 397 derived from load distribution by using a 95% confidence interval (shortest 95% confidence  
 398 interval as recommended by (ISO/IEC 2008) standard).

400 In addition to sources of variability in the models  $M2$  to  $M4$ , various sources of uncertainties  
 401 are taken into account in the simulation such as:

- 402 - Measurement uncertainties: the uncertainties in the measured value are assumed to be  
 403 normally distributed and independents with their standard uncertainty for:
  - 404 ○ Laboratory analyses: a relative standard deviation (%RSD) equal to 15%  
 405 (Gromaire and Chebbo 2001, Ruban et al. 2010);
  - 406 ○ Precipitation depth  $H_j$ : a %RSD equal to 10%;
  - 407 ○ Flow rate  $Q_{ij}$ : a %RSD equal to 10%;
  - 408 ○ Turbidity: a value of 10 FAU or 10 FNU was used as standard uncertainty  
 409 (Lacour et al. 2009, Metadier and Bertrand-Krajewski 2012).
- 410 - Prediction errors of the event volume (Model M1): this one was taken into account using  
 411 residual errors implied by the linear model established at a given site. Residual errors are  
 412 homoscedastic and normally distributed;
- 413 - Prediction errors of Turbidity-TSS correlation function  $f(T)$ .

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**Figure 6: Methodology for assessing pollutant annual loads**

418 The presented methodology has been implemented in Scilab®-5.4.1 open source software  
 419 (<http://www.scilab.org>). In the following section, results for TSS and TOC annual loads and  
 420 those obtained for the different pollutants are discussed. The calculation was performed for 2

421 years in *Sucy* and *Pin Sec* sites (2011 and 2012) and for 5 years in *Chassieu* site (2004 to  
 422 2008). To compare the results between the three sites, annual loads for each site are  
 423 normalized by active area (act.ha) and they will be called specific annual loads. The active  
 424 area  $S_{act}$  of a catchment is the area that really contributed to runoff. It was determined by the  
 425 area  $A$  of each catchment and the average runoff coefficient  $RC$  obtained using model M1 ( $S_{act}$   
 426 =  $RC \cdot Area$ , see *Table 1* and *Figure 2*).  $S_{act}$  is about 50 ha in *Sucy*, 55 ha in *Chassieu* and 8 ha  
 427 in *Pin Sec*.

## 428 APPLICATION ON THE THREE SITES

### 429 **Annual precipitations and volumes**

430 At the annual scale, the volumes ( $\sim$ net annual precipitation  $H_n = (\sum_j H_j - IL)$ ) expressed in mm  
 431 ( $\sim 10 \text{ m}^3/\text{act.ha}$ ) are shown in *Table 4*. The *Chassieu* site has an annual rainfall greater than  
 432 that precipitated in *Sucy* and *Pin Sec* sites, which will affect the annual volumes.

433

434

**Table 4 : Annual volumes on the three studied sites ( $\pm 95\%$  empirical confidence intervals)**

Site	Year	Annual volume $V_y/S_{act}$ (mm = $10 \text{ m}^3/\text{act.ha}$ )
<i>Sucy</i>	2011	$440 \pm 10$
	2012	$525 \pm 10$
<i>Chassieu</i>	2004	$810 \pm 15$
	2005	$580 \pm 15$
	2006	$690 \pm 10$
	2007	$775 \pm 10$
	2008	$840 \pm 10$
<i>Pin Sec</i>	2011	$515 \pm 10$
	2012	$530 \pm 10$

### 435 **TSS and TOC annual loads**

436 Specific annual loads of TSS and TOC, for 2 years in *Sucy* and *Pin Sec* sites and for 5 years in  
 437 *Chassieu* site are illustrated in *Figure 7(a, b)*.

438 The average values of TSS specific load in *Sucy* and *Pin Sec* sites (between 550 and 700  
 439 kg/act.ha/year) are lower than those of the *Chassieu* site (between 700 and 1100  
 440 kg/act.ha/year).

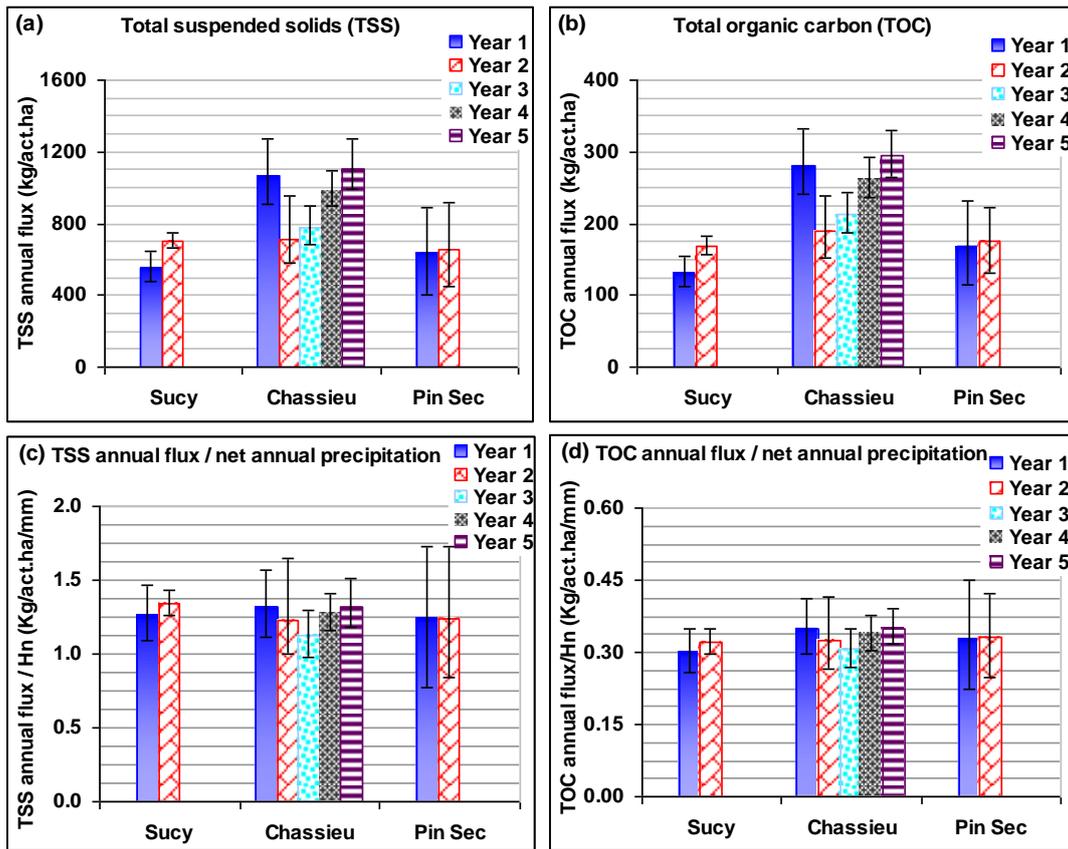


Figure 7: Annual loads at each site (average value from all simulations): (a) TSS annual loads; (b): TOC annual loads; (c) (respectively (d)): TSS (resp. TOC) annual loads per mm of water (net, see Table 4). Error bars represent the 95% empirical confidence intervals

Similarly, the same trend can be observed for TOC specific annual loads (between 130 and 175 kg/act.ha/year in *Sucy* and *Pin Sec* and between 190 and 295 kg/act.ha/year in *Chassieu*). At each site, uncertainties on TSS loads and TOC loads vary from one year to another depending on the amount of available data. This dispersion (around the mean value at 95% CI) varies from 5 to 15% in *Sucy* site, from 10 to 35% in *Chassieu* site and from 30 to 40% in *Pin Sec* site. Indeed, two factors affect the uncertainties of TSS loads on the same site: measurement uncertainties and those caused by selected models due to the absence of measurements. The effect of data reconstitution can be spotted on *Sucy* and *Pin Sec*, where fewer data is available in 2011 than in 2012 from flow rate and/or turbidity monitoring and in *Chassieu* where fewer data is available for 2004 and 2005 than for other years due to failures of the measurement system. In addition, the absence of a turbidity measurement in *Pin Sec* site involves uncertainties on the evaluation of annual loads higher than those observed in *Sucy* and *Chassieu* sites.

For temporal variations, we can observe a low inter-annual variability of TSS load with an apparent influence of meteorological conditions expressed as annual precipitation (Figure 7, (c)). Indeed, the annual load per mm water (net) represents a Site (discharge-weighted) Mean Concentration (SMC). So, the SMC during a given year will be

$$SMC(mg/l) \cong 10^2 \frac{M(kg/act.ha)}{H_n(mm)} \text{ (Equation 10). In other words, the overall TSS SMC is}$$

about  $130 \pm 15$  mg/l in *Sucy*,  $125 \pm 45$  mg/l in *Pin Sec* and  $125 \pm 20$  mg/l in *Chassieu* at a confidence level 95%. TSS SMC uncertainty in *Pin Sec* site is important ( $\sim \pm 35\%$ ) because it is derived from a small number of rainfall events ( $n=18$ ). This latter confirms the results of

467 (Mourad et al. 2005) which stressed that using fewer than 20 sampled rainfall events leads to  
468 uncertainties on TSS SMC above 30% (95% half-confidence interval).

469

470 Likewise, the overall TOC SMC is about  $31 \pm 4$  mg/l in *Sucy*,  $33 \pm 10$  mg/l in *Pin Sec* and  $33 \pm 5$   
471 mg/l in *Chassieu* at a 95% confidence level.

472 Low uncertainties in SS and TOC SMC in *Sucy* and *Chassieu* sites demonstrates that the use  
473 of turbidity monitoring, as indicator of TSS concentration, substantially improves the  
474 accuracy of evaluated annual pollutant load.

### 475 **Annual loads of micropollutants**

476 Annual loads of Pb,  $\sum$  OP,  $\sum_{16}$  PAH and  $\sum_9$  PBDE per active hectare are shown in *Figure 8*.  
477 The loads are presented for *Sucy* and *Pin Sec* sites. For *Chassieu* the PAH and PBDE loads  
478 are not calculated, due to limited number of sampled events. The annual loads of all studied  
479 pollutants for all years and their overall SMC are shown in *Table 5*.

480 We notice an interannual and intersite variability of annual pollutant loads, as for TSS annual  
481 loads. At each site, we observe an interannual variability influenced by meteorological  
482 conditions (*Table 4*). The inter-site variability of pollutants annual loads per mm water is  
483 logically linked to the calibration of distribution models of pollutants EMCs. Indeed, for  
484 pollutant displaying site-to-site differences between *Sucy* and *Pin Sec* sites ( $\sum_{16}$ PAH and  
485  $\sum_9$ PBDE (see *Figure 7* and *Figure 8 (c and d)*), pollutants annual loads per mm are different  
486 between sites. For example, in spite of similar annual precipitation, the  $\sum_{16}$ PAH loads in *Sucy*  
487 site are two times higher than those in *Pin Sec* site, but  $\sum_9$ PBDE loads in *Sucy* are ten times  
488 lower than those in *Pin Sec*, reflecting local contamination.

489 The Uncertainty on annual loads of different pollutants (at 95% CI) varies between 10 and  
490 60%, and may reach 100% as in the case of  $\sum_9$ PBDE in *Pin Sec* site (see *Figure 8 (d)*).  
491 Indeed, we can observe two types of the uncertainties of pollutants loads: i) Loads estimated  
492 using model M4: (taking into account the correlation between TSS and pollutant  
493 concentration for Zn, Cu, Cr, As, Ni, Pb, Sr, V,  $\sum$  NP,  $\sum_{16}$ PAH (*Sucy*) and  $\sum_{13}$ PAH (*Sucy*))  
494 have dispersion less than 30% around its average values; ii) By comparison those estimated  
495 from model M3 (pollutant uncorrelated with TSS like Cd, Co, Pt, Ti, Mo, BDE-209,  
496  $\sum_9$ PBDE, BPA,  $\sum$ OP,  $\sum_{16}$ PAH (*Pin Sec*),  $\sum_{13}$ PAH (*Pin Sec*)) have dispersion greater than  
497 30% around its average values and these uncertainties rise to more than 100% in some cases.  
498 This shows the importance of a continuous measurement of turbidity minimizing uncertainties  
499 in the estimation of annual loads of pollutants attached to solid particles. This point will be  
500 illustrated below to show the importance of considering the correlation between TSS and  
501 pollutant particulate concentration in the calculation method.

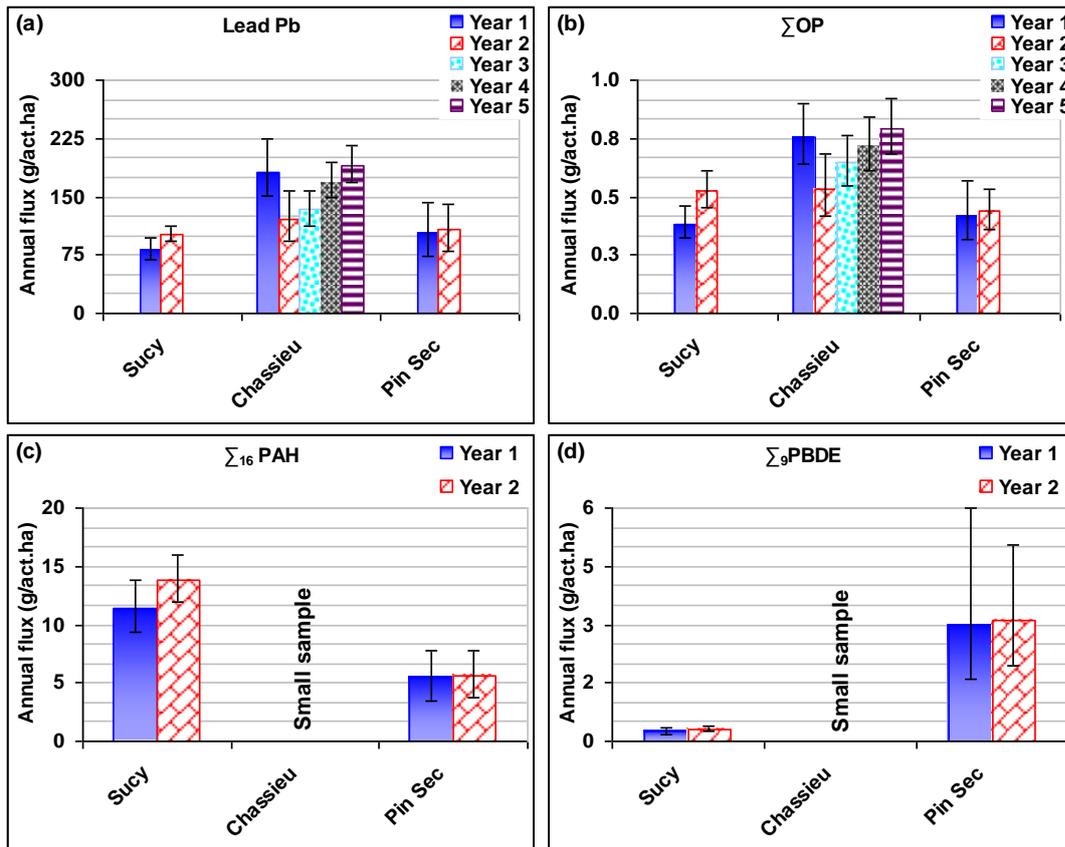


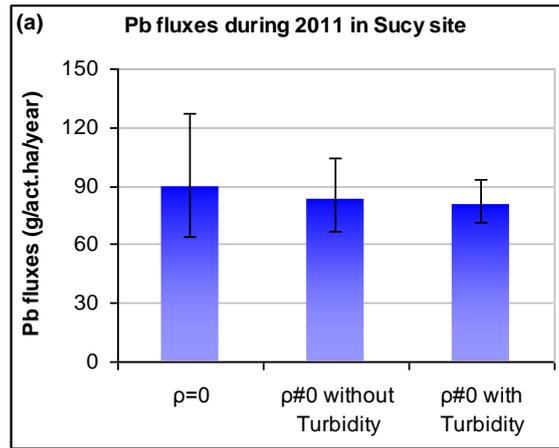
Figure 8: Annual loads at each site of: (a): Lead Pb; (b) sum of Octylphenols  $\Sigma$ OP; (c) sum 16 polycyclic aromatic hydrocarbons  $\Sigma_{16}$ PAH and (d) sum of 9 polybromodiphenylethers  $\Sigma_9$ PBDE. Error bars represent the 95% empirical confidence intervals. Years 1 and 2: 2011 and 2012 at Sucy & Pin Sec sites, and Years 1 to 5: 2004 to 2008 at Chassieu site.

### Efficiency of turbidity monitoring to reduce uncertainties in annual pollutant loads

To illustrate the impact of correlation  $\rho$  between  $TSS\ EMC$  and  $C_{P-Pol}\ EMC$ , three cases are simulated and compared for a pollutant having a particulate concentration highly correlated with the concentration of TSS (cases of lead *Pb* for example, see *Figure 4* and *Figure 8*): i)  $\rho$  considered as equal to 0 using model M3; ii)  $\rho$  considered with its actual value and using model M4 with TSS analyzed on water samples, iii)  $\rho$  considered with its actual value using model M4 with TSS assessed from continuous turbidity measurement. The uncertainties involved by the runoff model M1 can be neglected for comparison purpose: uncertainties obtained by this calculation are due only to errors from models M2 (TSS distribution) and M4 (solute distribution plus TSS correlation).

*Figure 9* show that this correlation changes the average annual loads as well as its uncertainties. We don't know the "exact value" of *Pb* annual load to validate the average *Pb* annual load obtained for each case. Anyway, the information provided by *Pb*-TSS correlation lowers the relative uncertainty on the annual concentration, especially if continuous monitoring if turbidity is available. The improvement of the uncertainty observed for case *ii* is explained by the number of events sampled for TSS analysis being larger than the number of events sampled for *Pb* analysis: 121 rainfall events vs. 24 sampled rainfall events.

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**Figure 9: Impact of the correlation between TSS EMC and pollutant particulate EMC with or without turbidity measurements (cases of lead Pb in Sucy site, year 2011)**

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**Table 5: Annual pollutant load per mm water for all years at each site and overall pollutant SMC. Each interval for pollutant load represents the 95% empirical confidence intervals. The intermediate value is the average value of load. \* SMC in µg/l. \*\*NE: No evaluated. \*\*\* SMC in ng/l**

Load (mg/act.ha/mm)	Pollutant	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Pt	Sr	Ti	V	Zn
<b>Sucy</b>	<b>2011</b>	[12;14;15]	[2;2.6;3.4]	[24;31;40]	[26;31;39]	[280;370;490]	[33;48;68]	[37;43;51]	[160;185;220]	[0.34;0.48;0.67]	[920;1085;1285]	[185;245;330]	[38;43;50]	[1530;1800;2120]
	<b>2012</b>	[14;15;16]	[2.3;2.8;3.4]	[28;33;40]	[30;33;36]	[330;380;450]	[40;54;74]	[42;47;53]	[180;195;215]	[0.42;0.54;0.72]	[1070;1220;1400]	[215;255;305]	[43;47;51]	[1760;1920;2110]
	<b>SMC*</b>	<b>1.4 ± 0.1</b>	<b>0.27± 0.04</b>	<b>3.2 ± 0.5</b>	<b>3.2 ± 0.4</b>	<b>38 ± 6</b>	<b>5.1 ± 1.4</b>	<b>4.5 ± 0.4</b>	<b>19 ± 2</b>	<b>0.05 ± 0.01</b>	<b>116 ± 12</b>	<b>25 ± 4</b>	<b>4.5 ± 0.4</b>	<b>187 ± 16</b>
<b>Pin Sec</b>	<b>2011</b>	[39;45;53]	[1.9;2.8;4.2]	[23;33;49]	[27;34;44]	[290;410;600]	[26;44;80]	[35;44;57]	[145;205;275]	[0.27;0.45;0.77]	[250;330;430]	[190;270;400]	[38;45;55]	[1590;1920;2360]
	<b>2012</b>	[41;46;51]	[2.2;2.8;3.7]	[26;33;43]	[30;35;41]	[325;413;535]	[31;45;67]	[38;44;53]	[150;200;265]	[0.32;0.45;0.65]	[275;330;395]	[215;270;355]	[40;46;52]	[1710;1940;2220]
	<b>SMC*</b>	<b>4.6 ± 0.4</b>	<b>0.28± 0.06</b>	<b>3.3 ± 0.7</b>	<b>3.4 ± 0.8</b>	<b>41 ± 10</b>	<b>4.5 ± 1.7</b>	<b>4.4 ± 0.9</b>	<b>20 ± 4</b>	<b>0.05 ± 0.02</b>	<b>33 ± 6</b>	<b>27 ± 7</b>	<b>4.5 ± 0.5</b>	<b>193 ± 28</b>
<b>Chassieu</b>	<b>2004</b>	[12;15;17]	[2.1;3;3.6]	[26;35;43]	<b>NE**</b>	[295;440;540]	<b>NE**</b>	[39;49;57]	[160;225;280]	[0.32;0.51;0.65]	[950;1220;1430]	[195;290;355]	[41;50;57]	[1710;2050;2340]
	<b>2005</b>	[10;14;16]	[1.5;2.8;3.6]	[19;33;42]		[210;410;520]		[32;47;57]	[110;210;270]	[0.23;0.5;0.66]	[770;1150;1400]	[140;270;350]	[34;47;56]	[1400;1940;2310]
	<b>2006</b>	[11;13;15]	[2;2.7;3.2]	[24;31;38]		[275;375;460]		[36;45;52]	[150;190;220]	[0.33;0.51;0.65]	[890;1095;1265]	[180;250;300]	[38;44;50]	[1570;1830;2050]
	<b>2007</b>	[13;14;16]	[2.2;2.9;3.4]	[26;34;41]		[330;425;495]		[38;48;55]	[180;220;240]	[0.33;0.51;0.64]	[975;1185;1360]	[215;280;330]	[43;49;54]	[1760;2000;2200]
	<b>2008</b>	[13;15;16]	[2.3;3;3.5]	[27;36;42]		[340;440;515]		[41;49;56]	[180;225;250]	[0.34;0.52;0.64]	[1020;1225;1400]	[220;290;345]	[44;50;56]	[1820;2070;2280]
	<b>SMC*</b>	<b>1.4 ± 0.1</b>	<b>0.29± 0.03</b>	<b>3.4 ± 0.4</b>				<b>42 ± 5</b>		<b>4.8 ± 0.4</b>	<b>21 ± 2</b>	<b>0.05 ± 0.01</b>	<b>118 ± 10</b>	<b>28 ± 3</b>

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Load (mg/act.ha/mm)	Pollutant	∑ <sub>16</sub> PAH	∑ <sub>13</sub> PAH	BDE-209	∑ <sub>9</sub> PBDE	BPA	∑OP	∑NP
<b>Sucy</b>	<b>2011</b>	[20;26;32]	[20;24;31]	[0.38;0.55;0.8]	[0.41;0.58;0.83]	[3.7;4.6;5.6]	[0.73;0.87;1.05]	[10;12;15]
	<b>2012</b>	[22;26;31]	[22;24;29]	[0.45;0.58;0.74]	[0.48;0.6;0.77]	[4.4;5.2;6.2]	[0.86;1;1.16]	[11;13;15]
	<b>SMC***</b>	<b>2600 ± 400</b>	<b>2400 ± 350</b>	<b>57 ± 10</b>	<b>59 ± 12</b>	<b>490 ± 65</b>	<b>95 ± 10</b>	<b>1240 ± 150</b>
<b>Pin Sec</b>	<b>2011</b>	[9;11;13]	[7;9;10]	[0.31;0.58;1.17]	[0.3;0.58;1.21]	[3.1;4.2;6]	[0.61;0.81;1.11]	[9;12;16]
	<b>2012</b>	[9;11;12]	[8;9;10]	[0.37;0.59;0.99]	[0.37;0.59;0.97]	[3.5;4.3;5.4]	[0.68;0.82;1.01]	[10;12;15]
	<b>SMC***</b>	<b>1060 ± 120</b>	<b>875 ± 100</b>	<b>58 ± 33</b>	<b>58 ± 35</b>	<b>430 ± 90</b>	<b>80 ± 15</b>	<b>1190 ± 250</b>
<b>Chassieu</b>	<b>2004</b>	<b>NE**</b>	<b>NE**</b>	<b>NE**</b>	<b>NE**</b>	[4;4.9;5.9]	[0.79;0.93;1.11]	[10;13;15]
	<b>2005</b>					[3.2;4.8;5.8]	[0.65;0.92;1.1]	[8;12;15]
	<b>2006</b>					[3.9;4.9;5.7]	[0.76;0.93;1.07]	[10;12;14]
	<b>2007</b>					[3.8;4.8;5.7]	[0.77;0.93;1.06]	[10;12;14]
	<b>2008</b>					[4;4.9;5.7]	[0.79;0.94;1.08]	[11;13;15]
	<b>SMC***</b>					<b>490 ± 50</b>	<b>95 ± 10</b>	<b>1240 ± 110</b>

## 532 **CONCLUSIONS**

533 A method was developed to set up annual pollutant loads and its uncertainties using a large  
534 dataset of pollutant EMC and continuous turbidity, flow rate and rainfall intensity recordings.  
535 This stochastic method is original and allows the coupling between a few event sampling  
536 campaigns and continuous measurements of hydrological and water quality parameters  
537 (rainfall intensity, flow rate, turbidity).

538 The results obtained can be summarized as follows:

- 539 - Lognormal distributions are well suited to describe pollutant EMC;
- 540 - The inter-annual variability of the pollutant annual loads in a given site are mainly  
541 influenced by weather conditions (annual precipitation);
- 542 - The inter-site variability of the pollutant annual loads per mm of water is related to the  
543 distribution of EMC of target pollutant.
- 544 - Annual loads of pollutants can be estimated with uncertainties ranging from 10% to 60%  
545 and can reach 100% for some pollutants. For the pollutants with a particulate fraction not  
546 correlated to TSS concentrations, the dispersion is greater than 30%. For the pollutants  
547 highly correlated with TSS concentration, this dispersion can be significantly reduced  
548 (10% to 30%) if we have information about TSS concentration (continuous measurement  
549 of turbidity).

550 A continuous measurement of turbidity can improve the estimation of annual loads of some  
551 pollutants attached to solid particles. Such results can be used to identify priority sources of  
552 pollution and then direct preventive / curative actions.

553 It would be worthwhile to pursue this line of research at other sites as a preliminary step to  
554 generalization.

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## 644 SUPPLEMENTARY MATERIALS

645 **Table 6: General characteristics of sampled rainfall events followed by a laboratory analysis in the three**  
646 **studied sites (min-max and median values) (Gasperi et al. 2014)**

	H <sup>1</sup> (mm)	Duration (h)	I <sub>mean</sub> (mm.h <sup>-1</sup> )	I <sub>max</sub> <sup>2</sup> (mm.h <sup>-1</sup> )	PDWP <sup>3</sup> (d)
<i>Sucy</i> (n=24)	1.2-38.6 8.43	0.6-26.3 7.9	0.4-3.8 1.5	2.4-24 7.9	0.17-9.18 2.1
<i>Chassieu</i> (n=7)	2.4-50.0 18.8	3.1-31.6 14.5	0.8-1.7 1.2	4.7-22.7 12.2	0.2-9.8 2.8
<i>Pin Sec</i> (n=18)	2.3-49.9 15.4	2.7-60.5 19.2	0.3-4.0 0.8	2.4-28.8 11.4	0.19-22.29 2.60

648 1) Precipitation depth; 2) I<sub>max</sub> evaluated over 5-min intervals; 3) Preceding dry weather period, in days. Min-Max  
649 values, as well as median values;  
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651 **Table 7: Pollutants analyzed and number of rainfall events (Gasperi et al. 2014)**

Groups (n=46)	Number of rainfall events	Substances and abbreviations
Metals (n=13)	Sucy: 8	Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), Platinum (Pt), Vanadium (V), Cobalt (Co), Molybdenum (Mo), Strontium (Sr), Titan (Ti)
	Pin Sec: 15	
	Chassieu: 5	
PAH (n=16)	Sucy: 8	Naphthalene (N), Acenaphthylene (Acyl), Acenaphthene (Acen), Fluorene (F), Phenanthrene (P), Anthracene (A), Fluoranthene (Fluo), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(cd)pyrene (IP), Dibenzo(ah)anthracene (DahA), Benzo(ghi)perylene (BPer)
	Pin Sec: 7	
	Chassieu: 4	
PBDE (n=9)	Sucy: 12	BDE-28 [tri], BDE-47 [tetra], BDE-99 [penta], BDE-100 [penta], BDE-153 [hexa], BDE-154 [hexa], BDE-183 [hepta], BDE-205 [octa], BDE-209 [deca]
	Pin Sec: 7	
	Chassieu: 2	
Bisphenol A and APnEOs (n=1+7)	Sucy: 12	Bisphenol A (BPA) Nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenol monocarboxylate (NP1EC), 4-tert-octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO)
	Pin Sec: 7	
	Chassieu: 2	

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**Table 8: Parameters of distributions in natural logarithm space ( $\mu$  and  $\sigma$ ) for models M3 ( $C_{T-pol}$  distribution) and M4 ( $C_{D-pol} + \tau$  distributionS). See equations 9 and 10 to switch from the logarithmic space to arithmetic space ( $m$  and  $SD$ ). Note: The units are given in the arithmetic space**

Model M3 : $C_{T-pol}$ (unit)						Model M4: $\xi$ (unit*/mg TSS) and $C_{d-pol}$ (unit)																
Substance	Sucy		Chassieu		Pin Sec		Substance	$\tau$ and $C_d$	Sucy		Chassieu		Pin Sec									
	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$			$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$								
Cd ( $\mu\text{g/l}$ )	-	0.81	pooled with Sucy *				TOC ( $\text{mg/l}$ )	$\tau$	1.58	0.21	pooled with Sucy											
Co ( $\mu\text{g/l}$ )	0.95	0.77						$C_{d-pol}$	1.53	0.75												
Pt ( $\mu\text{g/l}$ )	-	0.92					$\tau$	0.42	0.26													
Ti ( $\mu\text{g/l}$ )	2.98	0.84					$C_{d-pol}$	3.82	0.43													
Mo ( $\mu\text{g/l}$ )	1.15	0.98	Small sample: not processed				Cu ( $\mu\text{g/l}$ )	$\tau$	-1.28	0.43	Small sample: not processed											
$\sum_{16}$ PAH ( $\text{ng/l}$ )	M3 not relevant: $\rightarrow$ M4							6.90	0.47	$C_{d-pol}$					1.58	0.55	$\tau$	-3.52	0.27	M4 not relevant $\rightarrow$ M3		
$\sum_{13}$ PAH ( $\text{ng/l}$ )							6.70	0.48	$C_{d-pol}$	-1.21					0.52	$\tau$	3.00	0.52				
BDE-209 ( $\text{ng/l}$ )	3.70	0.99					5.47	1.40	$C_{d-pol}$	5.42					0.63	$C_{d-pol}$	5.42	0.63	3.85 0.58 0.78 0.37			
$\sum_9$ PBDE ( $\text{ng/l}$ )	3.64	1.00					5.48	1.39	$C_{d-pol}$	4.81					0.60	$\tau$	3.00	0.51				
BPA ( $\text{ng/l}$ )	6.00	0.62					pooled with Sucy	pooled with Sucy							As ( $\mu\text{g/l}$ )	$\tau$	-4.74	0.20	pooled with Sucy			
																$C_{d-pol}$	-0.48	0.17				
$\sum$ OP ( $\text{ng/l}$ )	4.39	0.55					pooled with Sucy	pooled with Sucy							Ni ( $\mu\text{g/l}$ )	$\tau$	-3.49	0.46	pooled with Sucy			
																$C_{d-pol}$	0.27	0.64				
$\sum$ NP ( $\text{ng/l}$ )															Pb ( $\mu\text{g/l}$ )	$\tau$	-1.90	0.42				
			$C_{d-pol}$	-0.66	0.63	$\tau$					-1.91	0.43										
$\sum$ NP ( $\text{ng/l}$ )							Sr ( $\mu\text{g/l}$ )	$\tau$	-1.91	0.43												
								$C_{d-pol}$	4.38	0.60					$C_{d-pol}$	0.31	0.49					
$\sum$ NP ( $\text{ng/l}$ )							V ( $\mu\text{g/l}$ )	$\tau$	-3.28	0.33												
								$C_{d-pol}$	0.76	0.20					$\tau$	0.76	0.20					
$\sum$ NP ( $\text{ng/l}$ )							$\sum$ NP ( $\text{ng/l}$ )	$\tau$	0.76	0.20												
								$C_{d-pol}$	6.45	0.65					$C_{d-pol}$	6.45	0.65					

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